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Advancements in analytical techniques for carbon nanomaterials

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ABSTRACT

With the mass production and application of carbon nanomaterials, effective detection and characterization methods in various media are crucial. This paper reviews commonly used techniques for analyzing carbon nanomaterials, starting with their separation and enrichment methods, including extraction and fractionation technologies. It then covers characterization techniques such as electron microscopy, spectroscopy, thermal analysis, electrochemical analysis, isotope labeling, imaging, fluorescence spectroscopy, laser-induced breakdown spectroscopy, mass spectrometry, scanning Raman microscopy, and quantitative analysis methods. The paper also introduces new carbon nanomaterials and specialized characterization methods, concluding with a discussion on future trends and prospects in the field.

Keywords: carbon nanomaterials; analysis method; carbon nanotubes; graphene; marking; imaging

1. Introduction

Carbon nanomaterials refer to carbon materials with at least one dimension in the nano scale (1–100 nm) in the dispersed phase. A variety of carbon nano materials, including carbon nanotubes (such as single-walled carbon nanotubes). Multi walled carbon nanotubes). Fullerene. Nano diamond. Carbon nanofibers. Carbon nano angle. Graphene. Mesoporous carbon. Carbon point. Carbon nanoparticles have been widely used in analysis and detection. Disease diagnosis. Biosensor. Tissue engineering and other different fields[1–6]. However, with the continuous increase of their production and application, their environmental release and potential human exposure are also increasing. Therefore, the safety and toxicity evaluation of carbon nanomaterials has become a hot topic in academia and society[7,8]. Since 2003, international science. Nature and other journals have published critical articles to discuss the potential negative effects of nanotechnology and nanomaterials on human health and living environment, and called for strengthening the research on the environmental behavior and toxicological mechanism of nanomaterials[9–11]. In order to achieve this goal, the innovation of analytical methodology is essential. Compared with traditional chemical pollutants, carbon nano materials have different properties, and traditional analysis methods are difficult to be directly applied to the analysis of nano materials. In recent decades, the research on the environmental behavior and biological toxicity of carbon nanomaterials has increased rapidly, but generally speaking, the research in this field is still

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in its infancy, the analytical methods are relatively scarce, and the accuracy and reliability of the methods need to be improved.

Size of carbon nanomaterials. Shape. Surface structure. Synthesis and purity. Stability and the interaction between materials and between materials and the environment are important physical quantities that need to be analyzed and characterized. In addition, it also has a small size effect. Surface and interface effects. Quantum size effect. Macroscopic quantum tunneling effect is the unique property of these nano materials[1,12]. The analytical methods of carbon nano materials can generally be divided into qualitative and quantitative methods. The qualitative method is mainly to analyze their morphology and components, and the quantitative analysis is mainly to characterize their concentration and quantity in different samples. This paper summarizes the methods and means of characterization and detection of carbon nanomaterials in recent years, and makes some prospects and thoughts, in order to further promote the improvement and standardization of analytical methods of carbon nanomaterials.

2. Sample pretreatment technology

Due to the complex matrix of actual samples, the sample pretreatment process is essential before the analysis of carbon nano materials. The core technology of sample pretreatment is the enrichment and separation process. In the process of separation, while excluding the interference of other substances, it is also required to keep the properties of nano materials unchanged. Based on the particularity of carbon nano materials, different extraction and separation methods need to be adopted according to different substrates. Generally, the first step is to stand. Centrifugation. Settlement. Filter and other methods to remove large particles for primary separation. If we want to separate carbon nano materials from a variety of materials, we need more technologies and means, such as extraction separation and fractional separation. Extraction separation has traditional liquid-liquid extraction. Solid phase extraction. Solid phase microextraction. Matrix dispersion solid phase extraction. Magnetic solid phase extraction and other methods[13]. Some relatively novel methods, such as cloud point extraction, on the basis of maintaining the original morphology of nanoparticles, can also overcome the interference of other heavy metal ions and organic matter to a certain extent, but it is difficult to exclude the influence of other nanoparticles and natural colloids[14]. The in-depth study of carbon nanoparticles also requires grading and separation of particles. First, surfactants need to be added to promote the dispersion of nanoparticles in solvents, and then grading nanoparticles through different fractionation methods. Common fractionation methods include the following: (1) field flow separation (FFF), which can achieve 1 nm–100 μm by combining the fluid and external electric field on the sampleμm macromolecules. Separation and purification of colloids and nanoparticles. (2) Chromatographic separation, such as liquid chromatography (LC). Size exclusion chromatography (SEC). Hydrodynamic chromatography (HDC), such as high performance liquid chromatography, can be used to separate C_{60} and C_{70} in fullerenes[15,16]. (3) Electrophoretic separation, including capillary electrophoresis. Gel electrophoresis. Isoelectric focusing and boundary electrophoresis are achieved by different migration rates of carbon nano materials under the action of electric field. (4) Other separation methods, such as disc centrifugation and even flow cytometry, can be used to separate carbon nanomaterials[17–19]. In the separation process of actual samples, it is usually necessary to combine a variety of separation methods to separate carbon nanomaterials in order to achieve the desired effect.

3. Analysis and characterization technology of carbon nano materials

The morphological characterization of carbon nanomaterials mainly uses electron microscopy, such as scanning electron microscopy. Transmission electron microscope. Optical microscope. Scanning probe microscope. Atomic force microscope and scanning tunneling microscope.

3.1. Transmission electron microscope

Transmission electron microscope (TEM) is to characterize the internal morphology of carbon nano materials by electron beam imaging of samples. Before the advent of computer-aided imaging, TEM images were usually used for qualitative analysis. As shown in **Figure 1**, Wilson et al. analyzed the structure of graphene oxide (go) through TEM, and showed that the carbon lattice at the bottom layer maintained the ordered arrangement and lattice position of graphene through electron diffraction, revealing that graphene monooxide thin sheets have good electron transparency and stability in electron beam[20]. With the emergence of modern image processing and pattern recognition technology, TEM image quantitative analysis technology came into being. Oshida et al. conducted quantitative analysis of micron and nano scale carbon materials through TEM and two-dimensional fast Fourier transform image processing technology[21]. Kehliu et al. also carried out quantitative analysis of carbon nanostructures through high-resolution TEM. The method includes two parts:digital image processing and lattice fringe characterization[22]. Gaddam et al. applied this method to the analysis of a variety of carbon nanostructures, such as graphene. The carbon structure of the model during the formation of soot[23] is shown in **Figure 2**.

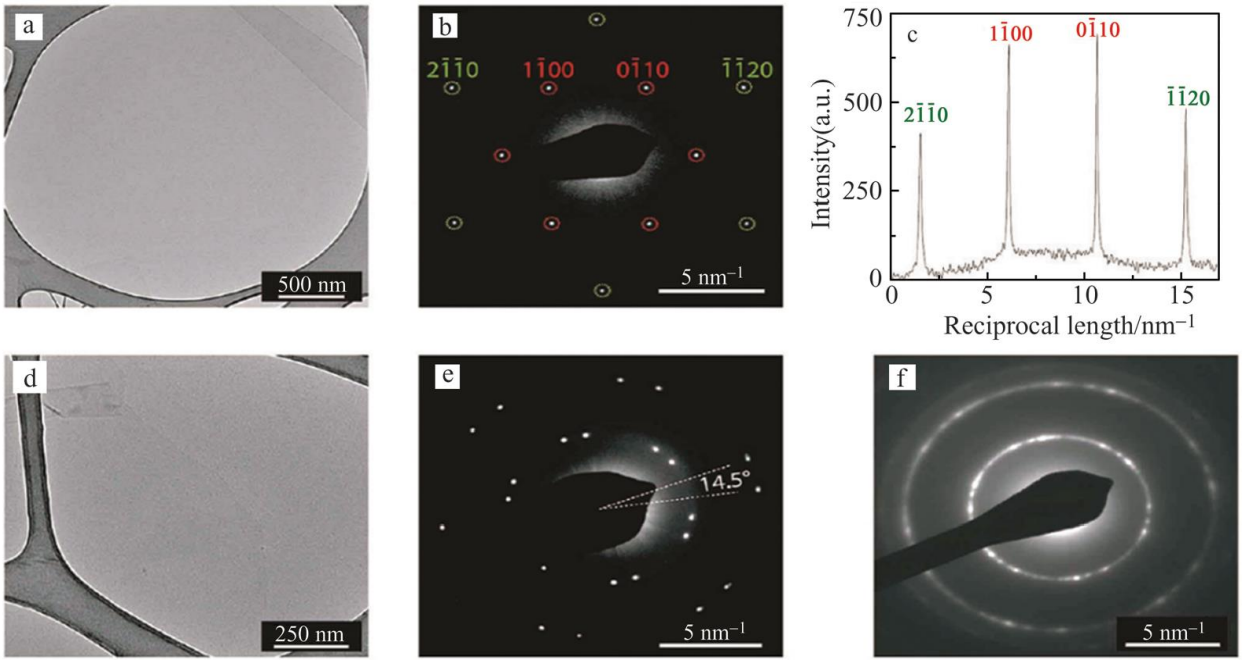

Figure 1. TE1VI and SAED image of a single GO sheet on a lacey carbon support[20].

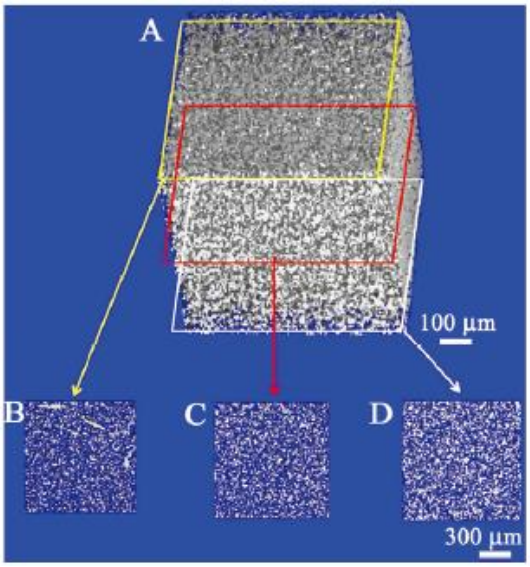

Figure 2. (A) Representative 3Dreconstructed microct image of unpurified MWCNT scaffold; and the **(B)** top; **(C)** middle and **(D)** bottom microct slice of the reconstructed 3-D MWCNT scaffold image[23].

High resolution TEM can also be combined with selected area electron diffraction (SAED) to further determine the crystal structure of carbon nano materials. For example, Yang et al. Found diamond deep inside carbon nano spheres in soil through saed, which (001). The three crystal planes (110) and (111) also prove that they have cubic structure, while nano diamond has (110), (111), (220) and (300) four crystal planes[24].

3.2. Scanning electron microscope

Scanning electron microscope (SEM) scans the surface of a sample by incident electron beam and interacts with it, so as to obtain the signal of surface atomic composition and distribution details. Because SEM can directly obtain the size distribution and morphology information of nano materials, it is used for different morphologies. Size characterization of carbon nanomaterials, such as carbon coils. Two dimensional or three-dimensional carbon nanoflowers, etc.[25–29]. The spatial resolution directly obtained by SEM can reach 1nm. For example, joner et al. Analyzed and characterized the microstructure of carbon nano materials generated during the combustion and pyrolysis of styrene butadiene rubber by SEM[30]. Recently, some studies have used SEM to analyze the composites and derivatives of carbon nano materials, such as the composites of carbon nanostructures and polymers. Graphene nanobelts. Carbon nanotubes filled with nanowires, etc.[31,32]. The combination of SEM and energy dispersive X-ray (EDX) analysis can dope carbon nano materials. Element composition and purity were further characterized[33,34].

3.3. Atomic force microscope and scanning tunneling microscope

Atomic force microscope (AFM) and scanning tunneling microscope (STM) are the means to characterize the morphology of solids by using the weak atomic force between the tip of atomic size and the sample surface, as well as the tunneling current generated by the tunneling effect[35–37], which can analyze the size and surface properties of carbon nano materials. In 2012, Brihuega et al. analyzed the essence and robustness of van Hoff singularity in the twisted layer of graphene through STM and theoretical calculation methods[38]. Reich et al. observed the effect of the amount of oxidant on graphene oxide through AFM and found that the thickness of graphene oxide prepared under different conditions was different, and the thickness gradually increased with the decrease of the amount of oxidant. Moreover, AFM can be used for statistical analysis of graphene oxide, which proves that the amount of oxidant plays a key role in its preparation, and provides a theoretical basis for improving the synthesis method of graphene oxide materials.

3.4. Spectral analysis

Spectral analysis mainly includes emission spectrum. Absorption spectrum and scattering spectrum. The commonly used analytical methods for carbon nano materials are absorption spectroscopy and scattering spectroscopy, such as UV visible absorption spectroscopy, Fourier infrared absorption spectrometry, X-ray absorption spectrometry, nuclear magnetic resonance spectroscopy and raman spectroscopy.

3.4.1. Ultraviolet visible absorption spectrum and Fourier infrared absorption spectrum

Carbon nanomaterials generally have π - π conjugated structure, so they have UV visible absorption. The position of the absorption peak is generally between 190–300 nm wavelength, for example, the UV absorption of ordered mesoporous carbon is about 270 nm. However, because many other substances will also produce UV absorption in this area, the information of carbon nano materials obtained by UV visible absorption spectroscopy is less, so it is generally only used as an auxiliary analysis means. Hagen et al. Linked the clear characteristics of the UV-vis-NIR spectra of independent single-walled carbon nanotubes (SWNTs) with the electronic excited states of a specific tube type by using the tight binding band structure calculation of the nearest neighbor jump integral related to chirality and diameter, and then assigned the (*n*, *m*) index to the interband transition of a specific tube type, thus realizing the quantitative analysis of the absorption spectrum. This method was used for rapid screening and optimization of sample composition in the synthesis of swnts[39]. The infrared absorption spectrum is mainly used to characterize the absorption of molecular vibration energy levels and the analysis of functional groups. For example, carbon nano materials with benzene rings will produce the skeleton vibration of benzene rings located at about 1500–1600 cm^{-1}. However, this signal is generally weak, so this method is generally only used to characterize derivatives and composites of carbon nanomaterials, such as graphene oxide. Amino and carboxylated graphene. Carbon nanobelts, etc.[40–42].

3.4.2. Fluorescence spectrum

The luminescence decay dynamics of the excited state of carbon nanomaterials is important for understanding its electricity. Optical and catalytic properties are of great significance[43]. Fluorescence lifetime. Time resolved fluorescence spectroscopy and imaging are the core of this process[44]. However, the fluorescence of the material itself is the premise of using this method for analysis, so this method is only applicable to graphene quantum dots. Analysis of carbon dots and multi walled carbon nanotubes with fluorescence. Magnus et al. studied the fluorescence lifetime fitting of two systems, one is homogeneous and near exponential fluorescein dyes, and the other is a highly heterogeneous system of graphene quantum dots[43]. The electronic transition of carbon dots can be observed in both single photon and two-photon excitation. It can be used to label cells, and then use confocal microscopy (single photon or two-photon excitation) for cell imaging analysis[45]. The fluorescence emission and quenching of carbon nanotubes have been measured by this method.

As shown in **Figure 3**, Wild and Jones directly detected and imaged the living roots of plants through a two-photon excitation microscope combined with the fluorescence of root canals and multi walled carbon nanotubes. Fluorescence spectroscopy can also be used to analyze the interaction between other substances and carbon nanomaterials[46].

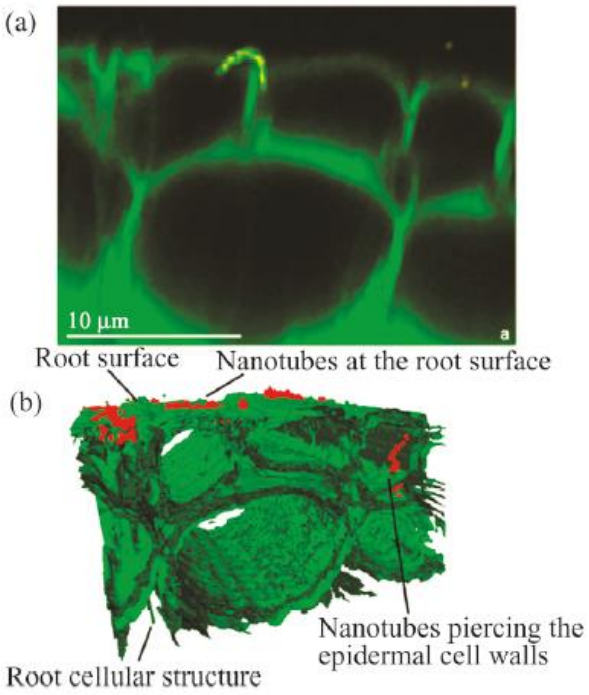

Figure 3. Mwcnts piercing the epidermal cellular structure[46]. **(a)** xz cross-sectional TPEM image showing both ends of a nanotube (orange) piercing the epidermal cell wall (green), the middle of the mwcnts is at the root surface; **(b)** A 3Dreconstruction of multiple xy TPEM sections showing mwcnts (red) at the root surface and piercing the epidermal cell walls of multiple cells (green).

3.4.3. Raman scattering spectrum

Raman scattering spectroscopy is widely used in qualitative and even quantitative analysis of various carbon nanomaterials because of its strong absorption peak specific to carbon skeleton. Raman scattering means that the photon energy of scattered light is different from that of incident light, which produces Stokes scattering with a frequency lower than that of incident light and anti Stokes scattering with a frequency higher than that of incident light. It depends on the structure of scattering molecules, so it can be used as the fingerprint spectrum of molecular vibration energy levels. For example, the characteristic Raman scattering peaks of nano diamond are located at 1140 cm^{-1} and 1470 cm^{-1}, while the characteristic peaks of fullerenes as allotropes are located at 305 cm^{-1} and 785 cm^{-1}. Moreover, Raman spectroscopy can also analyze the lattice integrity of nanocrystals. For example, the d-band peak generated by their lattice defects is located in the 1340–1360 cm^{-1} region[24]. Heise et al. found that the structure of multi walled carbon nanotubes is very similar to that of highly oriented pyrolytic graphite through Raman spectroscopy, proving the reliability of the ideal structure[47]. Graphene has the function of enhancing Raman scattering signal, which can be used for surface enhanced Raman analysis with single molecule sensitivity and chemical fingerprint recognition ability[48]. Raman scattering is also used to analyze the composites of carbon nanomaterials and their interactions with other compounds. For example, Liu et al. analyzed single-walled carbon nanotubes and three different target ligands through Raman scattering and found that connecting with different target ligands would significantly change the position and intensity of their Raman peaks[49]. Yang et al. provided the fingerprint of oxygen content change through the overtone region of Raman spectrum. The Raman radiation mode of graphene is complex and difficult to understand[50]. Budde et al. found the G and 2D Raman scattering angular distribution of graphene on glass by detecting the rear focal plane mode. G Raman radiation can be described by the superposition of two incoherent orthogonal dipoles on the graphene plane, which is of great significance for quantitative analysis of Raman spectral intensity under confocal microscope[51]. Raman spectroscopy can be further improved to achieve nano scale analysis. Saito et al. realized the nano scale spectral analysis of

graphene sheets through the tip enhanced near-field Raman, and the spatial resolution can reach 30 nm. The change of Raman band intensity generated from the near-field probe can easily estimate the edge boundary and the number of superimposed layers[52].

3.4.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) can not only characterize the elemental composition of carbon nano materials, but also explain the bonding state between atoms. For example, our research group analyzed different modified graphene by XPS combined with other characterization methods, and found that the modification of graphene changed its atomic hybrid form. Dispersion ability and self-assembly ability in water. Reunion trend[40]. The XPS absorption peaks of carbon nanomaterials are at 284.5 and 285.4, corresponding to the sp^2 and sp^3 hybridization of carbon. Different carbon nanostructures and their derivatives can be distinguished by the change of different hybrid proportions. For example, the change of oxygen content in graphene oxide films can be determined by XPS. XPS data processing requires peak splitting. Although there is an energy spectrum corresponding to it, there will be interference from human subjective factors, and the reliability and accuracy of the results need to be further improved. X-ray absorption spectroscopy can also be used to study the fine internal structure of carbon nanotubes.

3.4.5. X-ray diffraction

The lattice and crystal plane of carbon nano materials are mainly analyzed by X-ray diffraction (XRD). The X-ray diffraction ring can distinguish different carbon nano materials, especially nano materials with crystal structure, such as nano diamond. Both wide-angle diffraction and small angle diffraction are applicable to the analysis of carbon nano materials. The (111) crystal plane of nano diamond corresponds to the wide-angle diffraction peak at 44°[53], while the carbon nano belt only has the corresponding graphite peak at 26.7°, and it will change with the change of temperature[54]. The small angle diffraction peak of (100) crystal plane of ordered mesoporous carbon CMK-3 two-dimensional hexagonal space group is 1.04°, and the corresponding crystal plane spacing is 84.8 Å, while the small angle diffraction peak of (211) crystal plane of cmk-8 three-dimensional cubic Ia3d symmetry is 1.15°, and the corresponding crystal plane spacing is 77 Å[55].

3.5. Isotope labeling and imaging

In order to fully understand the biological effects and fate of carbon nanomaterials in the human body, including absorption. Distribution. Metabolism. Information such as toxicity requires accurate quantitative analysis of carbon nanomaterials. However, due to the interference of substrate carbon. Due to low occurrence concentration and lack of specific detection signals, it is very difficult to quantify carbon nanomaterials, especially in-situ quantitative analysis[56–58]. Therefore, highly sensitive and specific isotope labeling methods have been used for in-situ quantitative analysis of carbon nanomaterials. At present, a variety of isotopes have been used to label carbon nanomaterials, including ^{13}C, ^{14}C, ^{125}I, ^{131}I, ^{3}H, ^{64}Cu, ^{111}In, ^{86}Y, ^{99m}Tc and ^{67}Ga[59–68]. The labeling and detection process of non Carbon Radioisotopes is relatively simple, so it has become a commonly used isotope labeling method at present. They can be covalently bound. Chelation and encapsulation are labeled on the carbon skeleton. Due to the radioactive waste produced by radioisotope labeling and the stringent requirements of radioactive protection, non radioactive stable isotope ^{13}C labeling has also become another option. These labeled isotopes can be passed through liquid scintillation counters. Radiological imaging (e.g., Positron emission tomography-PET). Single photon emission computed tomography-SPECT). Isotope ratio mass spectrometry and other means to achieve real-time in-situ semi quantitative or even quantitative study of carbon nanomaterials in vivo.

However, the labeling process of isotope labeling is not only time-consuming, but also may change the properties of carbon nano materials, and the labeled isotopes also have the risk of falling off. These

shortcomings seriously limit the application of this technology in practical research. Therefore, Chen et al. used the intrinsic carbon cluster fingerprint signal of carbon nanomaterials in mass spectrometry to pair carbon nanotubes in mouse sub organs. Graphene oxide. Three carbon nano materials such as carbon dots were quantified, and their distribution in these sub organs was imaged by mass spectrometry[69]. Bussy et al. also imaged and chemically analyzed carbon nanotubes in macrophages through X-ray fluorescence microscopy[70], as shown in **Figure 4**.

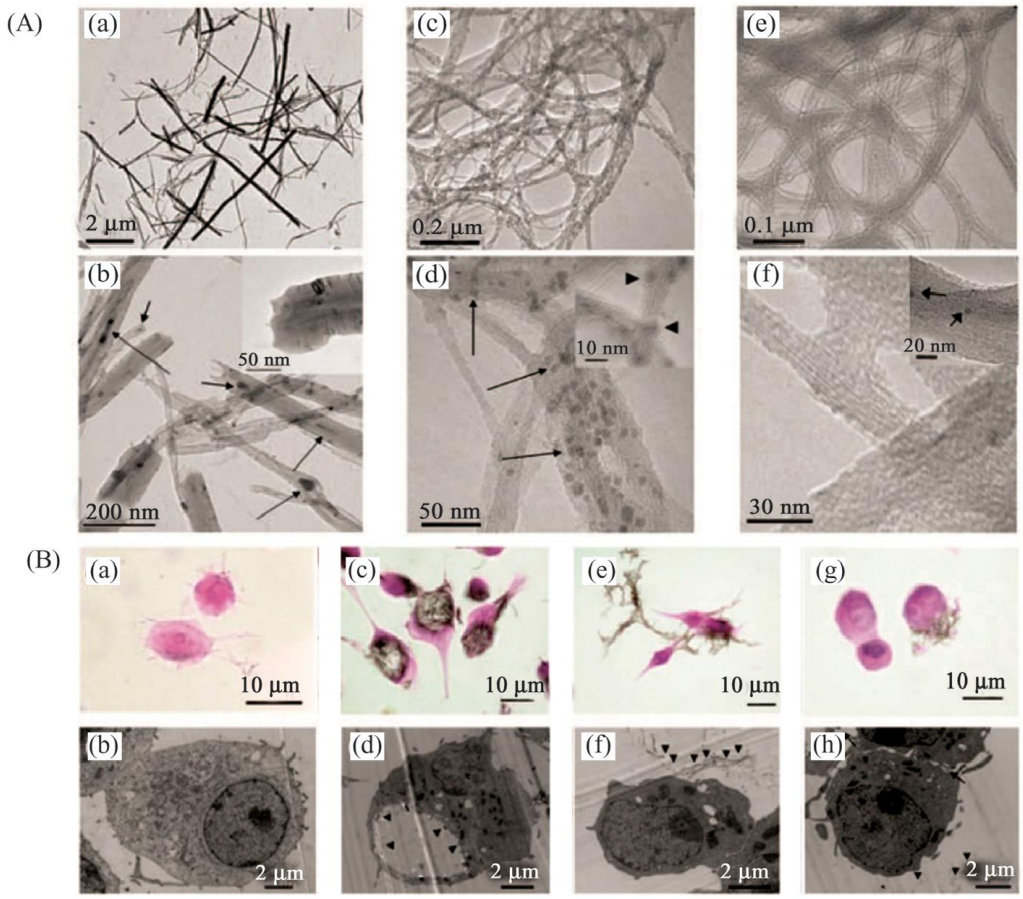

Figure 4. HRTEM images and X-ray fluorescence microscopy of cnts in macrophages[70]. **(A)** HRTEM images of mwcnts **(a** and **b)**, NP-swcnts **(c** and **d)**, and P-swcnts **(e** and **f)**; **(B)** Morphological and ultrastructural images of murin macrophages exposed to cnts, obtained by optical microscopy after hematoxylin-phloxin stain **(a, c, e,** and **g)** or by TEM **(b, d, f,** and **h)**. Nonexposed control macrophages **(a, b)**, Macrophages exposed to 10 Mg/mL mwcnts for 24 h **(c,d)**, Macrophages exposed to 10 Mg/mL NP-swcnts for 24 h **(e, f)**, Macrophages exposed to 10 Mg/mL P-swcnts for 24 h **(g, h)**.

3.6. Electrochemical detection method

Electrochemical analysis is an analytical method based on electrical response. The main electrochemical methods commonly used for detection are: cyclic voltammetry (CV). Linear sweep voltammetry (LSV). Open circuit potential time curve (OCP-T) and electrochemical DC polarization analysis[71]. Wang et al. proved by electrochemical method that graphene modified by nano diamond introduced the chemical fusion of nano diamond (NDS) and graphene lattice into the local pocket of sp^3 region. The existence of nano diamond will cause the conductive battery neck and affect the transmission. Graphene/nd films exhibit significant negative magnetoresistance at low temperature[72]. The determination of zeta potential is also an essential part to characterize the charging condition of carbon nano materials. Based on the small size effect and large specific surface area of carbon nano materials, there are often some oxidized or other functional groups on its surface, and there will be differences in zeta potential in solvents. Cioffi et al. studied carbon nano ferrocene complexes

by cyclic voltammetry and detected their voltage to the receptor system[73]. Zhang et al. used carbon nanomaterials as cathode coatings for degrading microbial contamination, and evaluated its semi quantitative performance and mechanism[74].

3.7. Thermal analysis

Thermogravimetric analysis and differential thermal analysis are commonly used in the thermal analysis of carbon nano materials. Doudrick et al. detected carbon nanotubes in cyanobacteria and urban air matrix through programmed thermal analysis, and proposed a set of temperature procedures to separate organic carbon and inorganic carbon, so as to quantify a wide range of carbon nanotubes[75]. Akbar studied the application of thermal analysis carbon nanotubes in industry, and studied the effect of magnetic field on the flow and heat transfer of carbon nanotubes in non-uniform tubes by using the creep flow model. It was found that single-walled carbon nanotubes and multi walled carbon nanotubes have a significant delay effect in water, and the physical properties of carbon nanotubes, such as velocity, are affected by its solid volume fraction. Gradient, etc.[76]. Bom et al. Studied the stability of oxidized multi walled carbon nanotubes through thermogravimetric analysis, providing evidence for the role of defect sites in carbon nanotubes, and proving that these defects can further enhance their stability in air through thermal annealing[77]. Kong et al. analyzed the principle of lattice thermal conductivity of single-layer and double-layer graphene[78]. Goli et al. proved that compared with ordinary copper films, copper graphene heterogeneous films have strong thermal conductivity by measuring the thermal diffusivity and thermal conductivity of graphene coated copper films[79].

3.8. Combination of various analysis methods

In the analysis of actual samples, it is often necessary to combine a variety of technical means to characterize carbon nanomaterials and their derivatives and composites in order to have a comprehensive understanding of its performance in all aspects[80]. For example, Gholampour et al. combined scanning electron microscopy. Energy dispersive X-ray spectrum. X-ray diffraction. Thermogravimetric analysis and Fourier transform infrared spectroscopy and other characterization techniques determine the distribution and mixing of reduced graphene oxide (RGO) in cement, and are related to the observed mechanical properties of RGO cement mortar composites. Through the test of axial tensile and shrinkage properties of cement-based composites, it is found that the oxygen content of RGO additives has an important impact on the mechanical properties of cement-based composites[81]. Jin et al. through zeta potential. Total reflection infrared spectrum. UV visible absorption spectrum. Optical microscope. Raman spectroscopy. The click chemistry of solvent dispersed and monolayer CVD grown graphene was studied by AFM and interaction energy analysis[82]. Lalwani et al. used spectral analysis. Electrochemical analysis. Imaging analysis by single wall carbon nanotubes. The porosity of three-dimensional all carbon scaffolds prepared from fullerene and even graphene. Structural integrity. The stability and conductivity were measured, and its physical properties were measured by nano indentation method[83].

3.9. Quantitative analysis

The rough quantification of carbon nano materials can use UV visible absorption spectrum, and its concentration change can be quantified according to the change of absorbance. For example, fullerene can be used to realize sediment by combining liquid chromatography with UV spectrophotometer. Bituminous coal. Bitumen. Separation and concentration quantification in samples such as carbon black[84,85]. However, the sensitivity and specificity of UV absorption are relatively lacking. Carbon nano materials with fluorescence absorption can also be quantitatively analyzed by fluorescence spectrophotometer, and the sensitivity and specificity can be correspondingly improved. Laser induced breakdown spectroscopy can quantify the concentration and particle size of carbon nanomaterials by changing the signal intensity of the emission

spectrum of the sample surface plasma. It does not need complex sample pretreatment process, and is often used for in-situ and in-situ online analysis. Because of its sensitivity and portability, microplasma spectroscopy has been used to measure the concentration of carbon aerosol in real time, and has more potential to be used for real-time online monitoring of other carbon nano materials. Scanning Raman microscope is also used for the quantification of carbon nano materials. Englert et al. Provided a systematic method based on scanning Raman microscope to quantitatively and reliably characterize the functionalized graphene, which was verified by thermogravimetry and mass spectrometry[86].

Mass spectrometry quantitative method is a reliable and accurate analysis method. High performance liquid chromatography and mass spectrometry have been successfully used for the separation and detection of carbon nano materials. For example, atmospheric pressure chemical ionization tandem mass spectrometry can be used for the quantitative analysis of fullerenes in plasma[87], while liquid chromatography electrospray ionization mass spectrometry can even be directly used for the quantitative analysis of C_60 in zebrafish embryos through the correction of internal standard $13c_60$[88]. Ku et al. Used differential mobility aerosol particle mass analyzer to characterize the structure of industrial carbon nanofibers in situ and determine its effective density. Fractional dimension and other properties, and provide a basis for its toxicological application[89]. Through qualitative and quantitative methods, Mazzuckelli et al. have successfully identified and characterized the potential sources of nanofibers exposed to workers during work[90].

3.10. Other analysis methods

In addition to the methods described above, there are also some emerging methods and means used for the quantification of carbon nanomaterials. For example, Tai et al. Reported a high resolution. The traceable electrospray spray differential mobility analysis method is used to quantitatively characterize the colloidal quantity, concentration and size distribution of graphene oxide nanoparticles. At the same time, it is proved that by changing the particle size distribution and concentration of graphene oxide nanoparticles (n-GOS), its colloidal stability and filtration efficiency can be effectively characterized[91]. Wang et al. quantitatively analyzed the n-type and p-type doped graphene sheets through the charge transfer of organic molecules, and proved that the charge transfer of organic molecules doped graphene is of great significance for the large-scale application of graphene based nano electrons in the future through theoretical and experimental results[92].

In addition, there are some calculation and simulation methods that can analyze some special properties of carbon nano materials. For example, Li and Chou analyzed the deformation of carbon nanotubes through the method of structural mechanics simulation. By calculating the elastic deformation of single-walled carbon nanotubes, it was revealed that the young's modulus of carbon nanotubes would not only change with the diameter of the tube, but also be affected by its helicity, which was verified by the experimental results[93]. Behfar and Naghdabadi[94] and He et al.[95] carried out nano scale vibration and resonance analysis of multilayer graphene sheets. Potts et al. theoretically analyzed the nanocomposites of reduced graphene oxide and natural rubber. Through the composite model, it was found that when the shape factor was equal to the length width ratio of the transmission electron microscope quantitative sheet, Guth equation was very consistent with the modulus data of the ground sample[96]. Song et al. analyzed the free vibration and buckling degree of the composite amount of multilayer graphene nanoplates through theoretical calculation and actual measurement, and found that it was randomLy oriented, and the concentration changed with the thickness of the beam[97]. Ouyang et al. further analyzed the microstructure and mechanical properties of such composites, and optimized the amount of graphene[98]. Cui and nasiri analyzed the signal transmission and stability of multilayer interconnected graphene nanoribbons, established a transmission line model, and conducted an in-depth study of its influence on the transmission rectangular pulse delay at the Fermi level[99,100]. Huang et al. calculated nitrogen through the first principle. The electronic properties of boron doped graphene clusters and their redox

catalytic activities were predicted and analyzed[101]. The magnetic properties of carbon nano materials are also the focus of attention. Palacios and Ynduráin conducted an in-depth density functional theory study on the spin resolved electronic structure of monatomic vacancies in monolayer and bilayer graphene, and conducted a critical analysis of vacancy induced magnetism[102]. Some carbon nanomaterials with special shapes, such as conical carbon nanofibers, a new type of carbon nanomaterials, have obtained its structure and growth mechanism by establishing its molecular model and structural analysis, measuring its conical vertex angle[103]. Fakhrabadi et al. further characterized its elastic and buckling characteristics through the method of molecular mechanics[104].

4. Conclusions and prospects

At present, there are various analytical methods for carbon nanomaterials, including electron microscopy. Absorption spectrum. Scattering and diffraction spectra. Techniques such as energy spectrum and mass spectrometry, as well as isotope labeling and imaging techniques. But at present, most methods can only be applied to the morphology of carbon nanomaterials. Dimensions. Qualitative analysis of quantum effect and Hall effect is still lacking in quantitative analysis methods. In addition, when analyzing complex environmental or biological samples, complex sample pretreatment processes, such as extraction and enrichment, are still needed. Classification treatment and other separation. Methods of purifying carbon nanomaterials. Therefore, in view of the existing problems, we put forward the following prospects for the development trend of analysis methods of carbon nano materials in the future:

(1) Development is simpler. Efficient sample pretreatment method. At present, the pretreatment process for carbon nano materials is the decisive step for the analysis of carbon nano materials. Simplifying or even eliminating the pretreatment process is to improve the detection efficiency. An important way to promote the development of analytical methods for carbon nanomaterials.

(2) A variety of methods are combined to complement each other. Mutual verification is also a development direction of carbon nano material analysis. Carbon nanomaterials have various and special properties, such as small size effect. Huge surface area. Surface and interface effects. Macroscopic quantum tunneling effect and other properties are difficult to be fully characterized by a single method. Therefore, the combination of multiple methods can not only overcome the one sidedness and uncertainty of a single method, but also be more comprehensive. It completely represents the properties of carbon nano materials.

(3) Analysis of carbon nanomaterials in more complex real samples. The concentration of carbon nanomaterials in actual environmental and biological samples is very low, so it is very difficult to analyze them. Only when it can be applied to the detection of carbon nanomaterials in real samples, can we have a more accurate understanding of their concentration in the actual environment and a more accurate assessment of human exposure risk.

(4) Development in situ. Online analytical methods for carbon nanomaterials. In situ testing. Online on-site monitoring has always been the goal of the development of analytical science, and it also puts forward higher requirements for the detection of carbon nano materials.

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Conflict of interest

The authors declare no conflict of interest.

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